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DEFECT LUMINESCENCE OF ORDERED PEROVSKITES A_2BWO_6

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This paper describes luminescence spectra of ordered perovskites of the type A_2BWO_6. The compounds A_2MgWO_6 show two different emission bands. From the Raman spectra of Ba_2MgWO_6 and Ba_2CaWO_6 and from luminescence experiments on $Ba_2Na_{0.8}W_{1.2}O_6$ and $Ba_2Ca_{0.95}Na_{0.04}W_{1.01}$ it is concluded that there is a slight deviation from complete ordering between the Mg^{2+} and W^{6+} ions in A_2MgWO_6.

1. Introduction

Owing to the simplicity of their crystal structure, compounds with ordered perovskite structure are particularly suitable as model compounds for fundamental studies of certain physical properties [1–4]. In our laboratory, research is carried out on the luminescence of compounds A_2BWO_6 in which A and B are bivalent ions. The A^{2+} ions are in 12-coordination (Ca^{2+}-site in perovskite, $CaTiO_3$). The B^{2+} and W^{6+} ions are in 6-coordination (Ti^{4+}-site in perovskite). The B^{2+} and W^{6+} ions are ordered in such a way that every WO_6 octahedron has only BO_6 octahedra as nearest neighbour [5]. Blasse and Corsmit [6] have reported the reflection spectra of compounds A_2MgWO_6 in which A is Ca, Sr or Ba, and of Ba_2BWO_6 in which B is Mg, Zn, Ca, Cd, Sr or Ba and the luminescence spectra of Ba_2MgWO_6. A remarkable phenomenon is the presence of two emission bands in their spectra of Ba_2MgWO_6. These bands have different excitation spectra. We have studied this double emission in more detail and extended the previous work to Ba_2CaWO_6, Ba_2SrWO_6, Ba_3WO_6, Sr_2MgWO_6, Sr_2CaWO_6, Ca_2MgWO_6 and Ca_3WO_6. These compounds have been described in the literature [5].

2. Experimental method

Samples were prepared by the usual techniques as described in ref. [7]. They were checked by X-ray powder analysis using Cu-Kα radiation. Excitation and emission spectra were recorded as a function of temperature on a Perkin Elmer MPF-2A spectrofluorimeter. The excitation spectra were corrected for the lamp intensity using lumogen as a standard. The emission spectra were corrected for the sensitivity of the photomultiplier according to the curve given by the manufacturer. Raman spectra were measured at room temperature on a Spectra Physics 700 Raman spectrometer using an argon ion laser (courtesy of Dr. J.H. van der Maas of this University).

3. Results

3.1. Luminescence spectra

The two emission bands which have been observed for Ba_2MgWO_6 are also present in the spectra of Sr_2MgWO_6 and Ca_2MgWO_6. By selective excitation it is possible to observe the two emission bands separately. The long-wavelength emission is observed when the sample is excited by long-wavelength UV radiation (320–340 nm), while the short-wavelength emission is observed when the sample is excited with radiation of 277 nm. Table 1 summarizes the results concerning the maxima of the spectra. In fig. 1 the emission bands of Sr_2MgWO_6 are reproduced. The long-wavelength emission is quenched at about 350 K, whereas the short-wavelength emission is already quenched at about 200 K. The two emission bands have different excitation spectra as reported in ref. [6]. Above 150 K the long-wavelength emission can also be excited in the excitation band of the short-wavelength emission. The excitation spectra of Sr_2MgWO_6 are reproduced in fig. 2. The emission spectra of Ba_3WO_6, Ba_2SrWO_6 and Ba_2CaWO_6 show only one band, the excitation spectrum of which resembles that of the short-wavelength emission of A_2MgWO_6.

Table 1
Maxima of the emission bands of compounds A_2BWO_6 at 5 K.

Compound	Luminescence excited in short-wavelength excitation band (nm)	Luminescence excited in long-wavelength excitation band (nm)
Ba_2MgWO_6	412	508
Sr_2MgWO_6	404	520
Ca_2MgWO_6	412	556
Ba_2CaWO_6	468	–
Sr_2CaWO_6	460 and 580	–
Ca_3WO_6	440 and 556	–
Ba_2SrWO_6	490	–
Ba_3WO_6	518	–

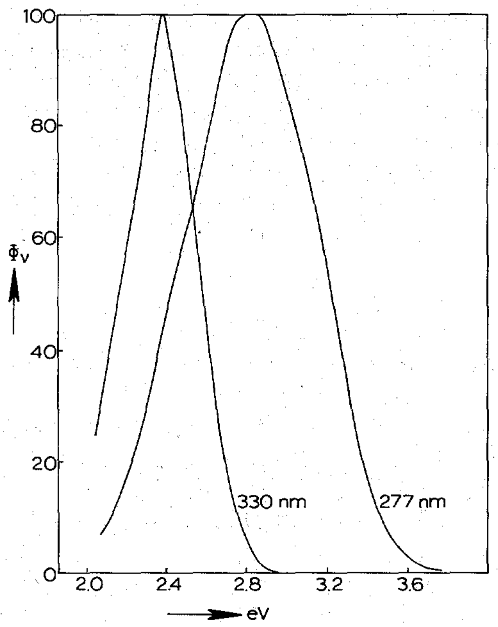

Fig. 1. Emission of Sr_2MgWO_6 at 5 K under 330 and 277 nm excitation respectively.

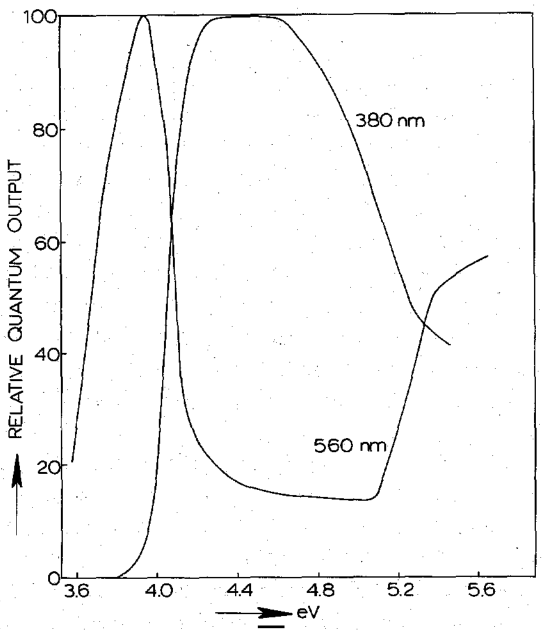

Fig. 2. Relative excitation spectra of the emission of Sr_2MgWO_6 at 380 and 560 nm at 5 K.

At temperatures below 50 K the compounds Ca_3WO_6 and Sr_2CaWO_6 show two emission bands, but this time it is the long-wavelength emission that appears at low temperature. Moreover, these emissions have practically the same excitation spectra which resemble strongly the excitation spectrum of the short-wavelength emission of A_2MgWO_6. For these reasons it is not very probable that the long-wavelength emission of Ca_3WO_6 and Sr_2CaWO_6 has the same origin as that of the A_2MgWO_6 compounds. The double emission of Ca_3WO_6 and Sr_2CaWO_6 is under investigation.

3.2. Raman spectra

For a number of samples of Ba_2MgWO_6 and Ba_2CaWO_6 prepared at a few different temperatures we measured Raman spectra under high resolution, in particular the spectral region around the ν_1 symmetric stretching frequency. The Raman spectra were not dependent on the way we prepared the samples within the experimental error. We found that the ν_1 peak of Ba_2MgWO_6 is considerably broader than that of Ba_2CaWO_6. The half-width values are 25 and 15 cm^{-1} respectively. We also measured Raman spectra of the compounds Sr_2MgWO_6, $SrCaWO_6$, Ca_2MgWO_6 and Ca_3WO_6, but the last three show a splitting of the threefold degenerate ν_3 peak. This points to a lowering of site symmetry. The half-width of the ν_1 peak for these compounds is about 20 cm^{-1}.

4. Discussion

Since the long-wavelength emission band of the compounds A_2MgWO_6 and the corresponding excitation spectrum are not observed in other tungstates with ordered perovskite structure, it is not likely that this emission band originates from a regular WO_6 octahedron. Contrary to the proposal of Blasse and Corsmit [6] it seems more acceptable that in addition to the regular, isolated WO_6 octahedra, there are other WO_6 octahedra which are crystallographically different from the regular ones. The relative broadness of the ν_1 peak in the Raman spectrum of Ba_2MgWO_6 points also in this direction. Since the ordered perovskite structure has only one crystallographic site for tungsten, we have to assume a deviation from the ideal structure. An obvious possibility is a slight deviation from complete order between the Mg^{2+} and W^{6+} ions. This order is stabilized by the difference between the charges and ionic radii of these ions. The radii difference is not very pronounced ($r_{Mg^{2+}}$ = 0.72 Å and $r_{W^{6+}}$ = 0.60 Å [8]); the charge difference, however, is very large. Nevertheless, the possiblity of a slight disorder is greater in compounds A_2MgWO_6 than in compounds with order between Ca^{2+}, Sr^{2+} or Ba^{2+} on one hand and W^{6+} on the other hand. Moreover, it has been shown that the ordered perovskites $SrLaMgNbO_6$ and $SrLaMgTaO_6$ (with equal ionic radii and charge difference 3 for Mg^{2+} and Nb^{5+} or Ta^{5+}) show a considerable deviation from complete order [9]. Since the X-ray diffraction spectra do not lead to the conclusion that there is disorder, this devia-

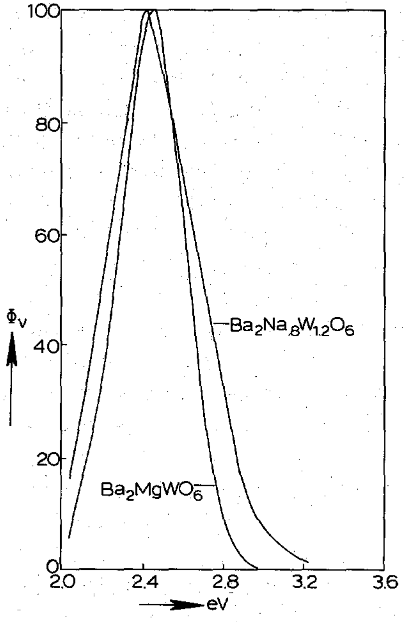

Fig. 3. Emission spectra of Ba_2MgWO_6 and $Ba_2Na_{0.8}W_{1.2}O_6$ under 320 nm excitation at 5 K.

tion from complete order is estimated to be less than about 2%. An attempt to prove the disorder by a calculation of the relative intensity of the (111) superstructure reflection failed because of the uncertainty in the position of the O^{2-} ions.

The assumed disorder, a mutual exchange of a Mg^{2+} and a W^{6+} ion, results in a number of WO_6 octahedra with other WO_6 octahedra as nearest neighbours. To test this hypothesis we prepared perovskites in which neighbouring WO_6 octahedra occur deliberately because of the stoichiometry. This is possible if we take for the B ion a univalent ion. So we prepared $Ba_2Na_{0.8}W_{1.2}O_6$ [10]. This perovskite shows a weak emission at very low temperatures (5 K). The emission resembles the long-wavelength emission of Ba_2MgWO_6 (fig. 3). Also, the excitation band is a combination of the short- and long-wavelength excitation band in Ba_2MgWO_6. Further, we prepared Ba_2CaWO_6 with an excess of tungsten by replacing part of the Ca^{2+} by Na^+ and W^{6+}: $Ba_2Ca_{0.95}Na_{0.04}W_{1.01}O_6$. This compound behaves completely analogous to Ba_2MgWO_6. There are two emission bands with different excitation spectra at 5 K. The long-wavelength emission is quenched at 330 K, whereas the short-wavelength emission which resembles the emission of Ba_2CaWO_6 is quenched at 200 K. At room temperature the long-wavelength emission can be excited in the short-wavelength excitation band. Thus the energy is transferred from the regular to the "defect" WO_6 octahedra. This is also true for Ba_2MgWO_6.

5. Conclusion

From our luminescence spectra we conclude that the long-wavelength emission observed in compounds A_2MgWO_6 originates from another centre than that for the short-wavelength emission. This disagrees with a proposal made previously by Blasse and Corsmit [6] who have suggested that both emissions are from one and the same regular WO_6 octahedron. From the broadness of the Raman ν_1 peak in Ba_2MgWO_6 compared to Ba_2CaWO_6 and the luminescence spectra of $Ba_2Na_{0.8}W_{1.2}O_6$ and $Ba_2Ca_{0.95}Na_{0.04}W_{1.01}O_6$, we tentatively conclude that the long-wavelength emission originates from defect WO_6 octahedra formed by mutual exchange of Mg^{2+} and W^{6+} ions. The degree of disorder must be small, because the X-ray spectra do not show any evidence for it. The luminescence from the defect WO_6 octahedra can also be excited in the regular WO_6 excitation band at not too low temperatures, so that energy transfer from the regular to the defect WO_6 octahedra is possible.

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